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Sr and Nd isotopic compositions of apatite reference materials used in U–Th–Pb geochronology

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ABSTRACT

Apatite is an important common U- and Th-bearing accessory mineral in igneous, metamorphic and clastic sedimentary rocks. The advent of *in situ* U–Th–Pb apatite geochronology by the SIMS and LA-(MC)-ICP-MS methods has demonstrated the importance of having uniform and homogeneous reference materials. Recently, it has been shown that Sr and Nd isotopic data combined with U–Pb age and trace element concentration data can provide important constraints on apatite paragenesis because this phase usually exhibits high Sr and REE concentrations but has low Rb/Sr ratios which result in negligible corrections for the ingrowth of radiogenic Sr. However, as apatite can potentially have complex internal structures resulting from multiple thermal events, such as inherited cores and metamorphic overgrowths, requires that the Sr and Nd isotopic data should be measured with high spatial resolution. However isobaric interferences hamper the precise determination of Sr or Nd isotopic compositions in LA-MC-ICP-MS analysis. In this work we undertook *in situ* measurements of Sr and Nd isotopic compositions of eleven apatite reference materials (AP1, AP2, Durango, MAD, Otter Lake, NW-1, Slyudyanka, UWA-1, Mud Tank, McClure Mountain and SDG) commonly used in U–Th–Pb geochronology. Our obtained Sr and Sm–Nd isotopic compositions for these apatite samples are consistent with those values obtained by solution-based methods (isotope dilution and ion chromatography) using MC-ICP-MS or TIMS, which demonstrates the reliability and robustness of our analytical protocol.

1. Introduction

Apatite [$Ca_5(PO_4)_3(F,OH,Cl)$] is a minor but ubiquitous mineral in diverse terrestrial and lunar rocks (Pan and Fleet, 2002; Poitrasson et al., 2002), and its major- and trace element compositions have been widely used in petrogenetic and mineral exploration studies (*e.g.* Sha and Chappell, 1999; Belousova et al., 2001, 2002; Chu et al., 2009a). It is becoming increasingly used in *in situ* U–Pb geochronology studies (Sano et al., 1999, 2006; Chew et al., 2011; Li et al., 2012; Thomson et al., 2012; Chew et al., 2014), while it has been long recognized that apatite can also provide important Sr–Nd isotopic petrogenetic information (Zaitsev and Bell, 1995; Rakovan et al., 1997). Typically its $^{87}Sr/^{86}Sr$ composition can be regarded as the initial strontium isotopic value because of the extremely low Rb/Sr ratio in most apatites (normally $^{87}Rb/^{86}Sr < 0.0001$). Recent developments in *in situ* laser ablation techniques make it possible to determine rapidly Sr (Bizzarro et al., 2003; Schmidberger et al., 2003; Horstwood et al., 2008; Nowell and Horstwood, 2009; Yang et al., 2009a,b; Henderson et al., 2010; Wu et al., 2010a,b,c; Mitchell et al., 2011; Wu et al., 2011, 2013a,b) or Nd (Foster and Vance, 2006; Foster and Carter, 2007; McFarlane and McCulloch, 2007, 2008; Yang et al., 2008; Carter and Foster, 2009; Gregory et al., 2009; Wu et al., 2010a,b,c; Mitchell et al., 2011; Wu et al., 2011, 2013a,b) isotopic compositions. Additionally, apatite has also been used to construct precise Lu–Hf isochrons due to its high Lu/Hf ratio (Scherer et al., 2001; Barfod et al., 2002, 2003, 2005; Soderlund et al., 2004; Amelin, 2005). It is increasingly recognized that apatite has wide applications in the Earth sciences, including geochronology, isotopic tracing and geochemical discrimination studies. Combined, these approaches can provide invaluable petrogenetic information.

Multi-collector thermal ionization mass spectrometry (TIMS) is still regarded as the benchmark method for Sr or Nd isotopic analysis owing to its inherent high precision (*e.g.* Li et al., 2007; Chu et al., 2009b). Nevertheless, this technique is significantly more time consuming compared to micro-beam methods (*e.g.* SIMS or LA-ICP-MS). Additionally the TIMS method is unable to detect spatial variations in isotopic compositions unless micro-drilling is employed. Recently, multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has become a routine tool for Sr or Nd isotopic measurements with the advantage of high sample throughput (Ehrlich et al., 2001; Waight et al., 2002; Fortunato et al., 2004; Balcaen et al., 2005; Yang et al., 2011c).

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Additionally, when coupled to laser ablation (LA) systems, *in situ* MC-ICP-MS analysis makes it possible to obtain rapidly Sr or Nd isotopic data from Sr- or REE-enriched minerals. While the precision of Sr or Nd data obtained by LA-MC-ICP-MS cannot compare with that of TIMS, sample preparation is much easier and the sample throughput is significantly higher (*e.g.* Adams et al., 2005; Hart et al., 2005; Jackson and Hart, 2006; Balter et al., 2008; Copeland et al., 2008; Fietzke et al., 2008; Richards et al., 2008; Simonetti et al., 2008; Vroon et al., 2008; Richards et al., 2009; Copeland et al., 2010; Yang et al., 2011a; Guo et al., 2014; Yang et al., 2014a).

Similar to *in situ* Hf isotopic analyses on zircon (Woodhead and Hergt, 2005; Wu et al., 2006; Blichert-Toft, 2008; Fisher et al., 2011a) or *in situ* Pb isotopic analyses on K-feldspar (Tyrrell et al., 2006), matrix-matched reference materials are required for *in situ* Sr or Nd analyses (Yang et al., 2009a; Wu et al., 2010a,b,c). Undoubtedly, some apatite reference materials employed in U–Th–Pb geochronology studies using the SIMS or LA-MC-ICP-MS techniques have potential as *in situ* Sr or Nd reference materials. Nevertheless, their suitability as apatite Sr or Nd reference materials has not been investigated in detail, with only a few Sr and Nd isotopic data available for Durango apatite (Foster and Vance, 2006; McFarlane and McCulloch, 2008; Fisher et al., 2011b; Hou et al., 2013; Kimura et al., 2013a,b). Other apatite reference materials (*e.g.* AP1, AP2, MAD, Otter Lake, NW-1, Slyudyanka, UWA-1, Mud Tank, McClure Mountain and SDG) have not been investigated for their Sr and Nd isotopic compositions, although their U–Th–Pb age systematics have been well characterized using SIMS (Sano et al., 1999; Nishizawa et al., 2004; Frei et al., 2005; Sano et al., 2006; Li et al., 2012), LA-ICP-MS (Chew et al., 2011, 2014) or LA-(MC)-ICP-MS (Willigers et al., 2002; Thomson et al., 2012). Therefore, more data and inter-laboratory comparisons are required to evaluate the suitability of apatite age reference materials as potential Sr or Nd reference materials.

In this paper, we first present our Sr and Nd isotopic analyses for MAD, Otter Lake, NW-1, Slyudyanka, Durango, UWA-1, Mud Tank, McClure Mountain and SDG apatite using both solution-based and laser-ablation sampling techniques in our laboratory. Additionally, the suitability of two gem quality apatite megacrysts (AP1 and AP2), probably from Madagascar, was also evaluated for use as our *in-house* Sr or Nd apatite reference materials. The Sr and Nd isotopic compositions obtained for these natural apatite samples are all consistent with values obtained by solution-based methods (isotope dilution and ion chromatography) using MC-ICP-MS or TIMS, which indicates the reliability and robustness of our analytical protocol.

2. Analytical methods

All eleven apatite samples investigated in this work were embedded in epoxy resin blocks and polished prior to being analyzed for their major and trace element concentrations and their Sr and Nd isotopic compositions using *in situ* techniques. To validate the reliability of the *in situ* analyses, the Sr and Nd isotopic compositions of aliquots of the eleven apatite reference materials were also analyzed by ID-TIMS or ID-MC-ICP-MS. All analyses were conducted at the State Key Laboratory of Lithospheric Evolution, the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing.

2.1. Major and trace element analyses

Major element analyses were conducted by electron microprobe analysis (EMPA) using a JEOL–JAX8100. The typical beam size was 20 μm and an accelerating voltage of 15 kV and a beam current of 20 nA were employed. Counting times were 20 s and total Fe is expressed as Fe_2O_3. Analyses were acquired using the Probe for Windows software and X-ray correction was undertaken using the CITZAF software. The analytical uncertainties are within 2% for TiO_2 and CaO, but are ~10–20% for other elements due to their low concentrations.

In situ trace element concentration analyses of individual apatite grains were conducted using an Agilent 7500a quadruple inductively coupled plasma mass spectrometer (Q-ICP-MS) coupled to a 193 nm excimer ArF laser ablation system. The analytical protocol employed is similar to that outlined in Xie et al. (2008). Helium gas was flushed to minimize aerosol deposition around the ablation site, and mixed with argon gas downstream of the ablation cell. During analysis, a spot size of 30 μm was applied with a repetition rate of 6 Hz, and the energy density employed was ~10 J/cm^2. All measurements were performed in time-resolved analysis mode utilizing peak jumping with 1 point per mass peak. Each spot analysis consisted of approximately 30 s of background acquisition and 60 s of sample data acquisition. Every five sample analyses were followed by one NIST SRM 610 measurement. Raw counts were processed offline and data-reduction and concentration calculations were then performed using the Glitter laser ablation software (Griffin et al., 2008). For calibration purposes, Ca determined by electron microprobe, was used as an internal standard.

2.2. In situ Sr isotopic analyses

In situ Sr isotopic measurements by MC-ICP-MS have already been described in detail elsewhere (Yang et al., 2009b), hence only a brief description is given below. A spot size of 60–120 was employed with a 6–8 Hz repetition rate and an energy density of 10 J/cm^2, depending on the Sr concentration of the samples. The Sr isotopic data were acquired by static multi-collection in low-resolution mode using nine Faraday collectors. Prior to laser analyses, the Neptune MC-ICP-MS was tuned using a standard solution to obtain maximum sensitivity. A typical data acquisition cycle consisted of a 40 s measurement of the Kr gas blank with the laser switched off, followed by 60 s of measurement with the laser ablating. As will be discussed below, AP1 has a nearly uniform Sr isotopic composition. Every ten sample analyses were followed by one AP1 apatite reference material measurement for external calibration. Meanwhile, AP2 apatite was analyzed in each analytical session and treated as an unknown sample during the data-reduction procedure.

Data reduction was done offline and the potential isobaric interferences were accounted for in the following order: Kr, Yb^{2+}, Er^{2+} and Rb. Firstly, the interference of ^{84}Kr and ^{86}Kr on ^{84}Sr and ^{86}Sr, respectively, was removed using the 40 s Kr gas baseline measurement. The isobaric interference correction of ^{84}Kr and ^{86}Kr on ^{84}Sr and ^{86}Sr was conducted using the natural Kr isotopic ratios ($^{83}Kr/^{84}Kr = 0.20175$, $^{83}Kr/^{86}Kr = 0.66474$) (Christensen et al., 1995; Bizzarro et al., 2003). Secondly, the presence of $^{167}Er^{2+}$, $^{171}Yb^{2+}$ and $^{173}Yb^{2+}$ at masses 83.5, 85.5 and 86.5 was monitored based on the protocols of Ramos et al. (2004). Using the isotopic abundances of Er and Yb (Chartier et al., 1999), the potential double-charged ion isobaric interference of $^{166}Er^{2+}$ (at m/z 83), $^{168}Er^{2+}$ (at m/z 84) and $^{170}Er^{2+}$ (at m/z 85) on $^{83}Kr^{+}$, $^{84}Sr^{+}$ and $^{85}Rb^{+}$, respectively, was evaluated and corrected by monitoring the interference-free $^{167}Er^{2+}$ (at m/z 83.5) signal intensity. Similarly, the potential double-charged ion isobaric interference of $^{170}Yb^{2+}$ (at m/z 85), $^{172}Yb^{2+}$ (at m/z 86), $^{174}Yb^{2+}$ (at m/z 87) and $^{176}Yb^{2+}$ (at m/z 88) on $^{85}Rb^{+}$, $^{86}Sr^{+}$, $^{87}Sr^{+}$ and $^{88}Sr^{+}$, respectively, was assessed and corrected for by monitoring the interference-free $^{173}Yb^{2+}$ (at m/z 86.5) signal intensity (Yang et al., 2014b). Thirdly, the natural ratio of $^{85}Rb/^{87}Rb$ (2.5926) was used to correct for isobaric interference of ^{87}Rb on ^{87}Sr by the exponential law, assuming that Rb has the same mass discrimination behavior as Sr (Christensen et al., 1995; Ehrlich et al., 2001; Bizzarro et al., 2003; Ramos et al., 2004, 2005; Woodhead et al., 2005; Richards et al., 2008; Yang et al., 2011a, 2012). It is observed that the obtained $^{87}Rb/^{87}Sr$ ratio is typically less than 0.0005 during *in situ* apatite Sr analysis, indicating that the radiogenic ^{87}Sr contribution is negligible (Yang et al., 2011a). In addition, our previous work demonstrated that Ca argides and dimers had an insignificant influence on Sr isotope analysis using a Neptune MC-ICP-MS (Yang et al., 2011c), a conclusion that is also strongly supported by other studies (Bizzarro et al., 2003; Ramos et al., 2004; Yang